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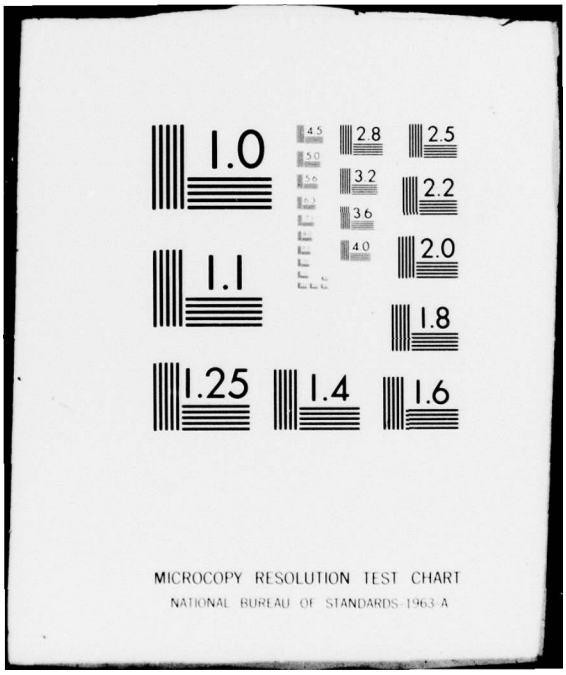
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This report summarizes the accomplishments of the work concerning vacancies in aluminum. A program of theoretical calculations was conceived and carried out. Mathematical details are contained in the several publications that have resulted from this work. This account is intended to enable the reader to place the work in general perspective. A list of the publications which can be consulted for more specific information is included at the end of this narrative.

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FORMATION AND MIGRATION ENERGIES OF VACANCIES AND INTERSTITIAL DEFECTS IN ALUMINUM

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Submitted to

Army Research Office

May 1979

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The purpose of this report is to summarize the accomplishments of the work at LSU supported by ARO concerning vacancies in aluminum. An ambitious program of theoretical calculations was conceived and carried out. Mathematical details are contained in the several publications that have resulted from this work, and will not be reported here. This brief account is intended to enable the reader to place the work in general perspective. A list of the publications which can be consulted for more specific information is included at the end of this narrative.

The general structure of our work is outlined schematically in Fig. 1. The problem of studying the electronic structure of a vacancy can be divided into two major parts: (1) determination of the change in the crystal potential produced by the defect, and (2) solution of the resulting Schrodinger equation. The first part is the most complicated, and involves both the most interesting physics and the most serious uncertainties.

The determination of the change in potential involves the following steps.

1. Locate the position of the atoms around the defect. This requires a study of the relaxation of atoms in the vicinity.

2. Find the electron charge distribution on these atoms. This requires a first principles self-consistent band calculation.

3. Construct the defect potential from the charge distribution. The crystal responds to the defect potential by a further alteration of charge density near the defect. This self-consistent readjustment is described by the wave vector dependent dielectric matrix, and leads to a screened defect potential.

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Finally, we solve the effective Schrodinger equation using a method based on scattering theory, without introducing any restrictive assumptions of spherical symmetry of the defect potential.

The calculations were much more complete and rigorous than any previously attempted. Several of the steps mentioned above required extensive subsidiary calculations. Significant contributions to the physics of metals resulted from these intermediate calculations which can be applied in contexts quite remote from the defect problem.

Our work began with an investigation of atomic relaxation around a vacancy and an interstitial. In the former case, it was possible to use experimentally observed lattice vibration spectra to determine atomic force constants out through the 8'th shell of neighbors. The method of lattice statics was then applied to find the atomic displacements. In the case of an interstitial, one must calculate the forces between atoms at distances closer than are found in the normal bulk solid. It is unwise to rely on lattice vibration spectra for information in such circumstances. For this reason, we determined a pseudo potential which reproduced the lattice vibration spectrum quite well, but which could be used for the calculation of interatomic forces at moderately short distances. A substantial amount of lattice distortion (17% outward displacement of first neighbors, for example) was found to occur around an interstitial impurity.

At this point, it was decided to base our further work on vacancies on a fully first principles band calculation, rather than on the pseudopotential or jellium models in common use. This was done, and the work which we describe here was the first calculation of this type to be performed.

With this objective in mind, it was then necessary to make a self-consistent calculation of energy bands in aluminum. This was carried out using the LCGO (linear combination of Gaussian orbitals) method, and the Kohn-Sham exchange potential. The Fermi surface was computed and found to be in good agreement with experiment. The X-ray form factors which are Fourier coefficients of the charge density were also found to agree well with experiment.

Knowledge of the charge density around an atomic site enables us to start the computation of the change in the crystal potential when an atom is removed. It is necessary, however, to be able to determine the redistribution of charge which occurs when an atom is removed. In many previous calculations, this has been estimated using the dielectric function for a free electron gas of the appropriate density. We decided to improve this aspect of the investigations by calculating and using the full dielectric function matrix for a perfect aluminum crystal.

The calculation of the dielectric function matrix was of major importance in itself and we shall describe briefly here some of the more important aspects of this work. In the first place, we developed the formal theory of the dielectric function to be employed when the calculation is based on energy bands and wave functions using a local density dependent exchange-correlation potential. It is not necessary either to neglect exchange corrections to the dielectric matrix or to include corrections in an ad hoc way. In fact, the local density approximation can be used to determine a specific and unambiguous exchange correction. We used this formalism and our calculated bands and wave functions to calculate the frequency and wave vector dependent dielectric matrix. This

calculation was also the first of its type for a real metal.

It has proved to be possible to compare the dielectric matrix directly with experiment. We were able to account for some low energy loss peaks observed when fast electrons pass through aluminum. These peaks result from indirect interband transitions, and are found theoretically when the energy loss function is computed from the dielectric matrix. This successful comparison of theory and experiment increases confidence that the dielectric matrix is essentially correct. In addition, we have been able to determine the bulk plasmon energy, width, and the dispersion of these quantities with respect to wave vector as well. The results can be compared with experiment. These calculations are now being prepared for publication. We are not aware of previous calculations of the plasma dispersion relation on the basis of first principles band calculations.

The change in the crystal potential due to the introduction of a vacancy was obtained combining the negative of the contribution to the crystal potential from the missing atom plus that due to inward displacement of the potentials of the first two shells of neighbor atoms. The result is screened by the dielectric function matrix. We now proceed to calculate the change in the sum of single particle energies. This can be expressed in terms of an integral of the sum of the scattering phase shifts over all occupied states:

$$\Delta E_{sp} = -Z\ E_F^o - \frac{2}{\pi}\int_{E_o}^{E_F^o} \delta(E)dE \qquad (1)$$

in which E_F^o is the Fermi energy, Z is the valence, and E_o is the energy of the

lowest state in the band. The computation of the phase shift does not require any assumption of spherical symmetry of the defect potential. The formal relation is

$$\delta(E) = -\mathrm{Im}\ \ell n\ \det[I-GV] \tag{2}$$

in which G is the Green's function matrix,

$$G = \lim_{\varepsilon \to 0^+} \frac{1}{E+i\varepsilon-H_o} \ , \tag{3}$$

E is the energy of an occupied state, and H_o is the perfect crystal Hamiltonian. The matrix V in (2) represents the defect potential.

The matrices representing these operators were computed numerically. The basis functions employed were the 52 independent Gaussian orbitals used in the energy band calculation, placed on thirteen sites, comprising the central cell and its twelve nearest neighbors. Thus the matrices of G and V have dimension 676x676, and special numerical techniques had to be employed to calculate the phase of the determinant in (2). We believe that in terms of the size of the basis employed, the present work is the most complete calculation of defect energies that has been performed.

The value for the net change in single particle energies was found to be 2.84 Ry. This can be compared with the sum of single particle energies in the perfect crystal, which can be found using our computed density of states to be 2.39 Ry. The difference of these quantities, 0.45 Ry (6.1 eV) is a first,

crude approximation to the vacancy formation energy at constant volume. The most recent experimental value of the formation energy is 0.69 ± 0.03 eV.

In fact, the change in the sum of the single particle energies is not the vacancy formation energy. All theories which include electron-electron interactions, however approximately yield expressions for total energies which differ from the sum of single particle energies by corrections which compensate for the overcounting of electron interactions which arises when the one particle eigenvalues are summed. A relatively simple formal expression exists for this difference in the local exchange approximation on which the present work is based.

Total energy = sum of single particle energies

$$- \frac{1}{2} e^2 \int \frac{\rho(\vec{r})\rho(\vec{r}')}{|r-r'|} d^3r' - \frac{1}{4} \int \rho(r) V_{ex}(r) d^3r$$

$$+ \frac{Z^2 e^2}{2} \sum_{\mu \neq \nu} \frac{1}{|R_\mu - R_\nu|} \qquad (4)$$

in which $\rho(r)$ is the electron density, and V_{ex} the Kohn Sham exchange potential,

$$V_{ex} = -2e^2 \left(\frac{3\rho}{8\pi}\right)^{1/3} . \qquad (5)$$

Unfortunately, we are unable to compute the change in these correction terms within the framework of the present calculations because of difficulties in obtaining the change in the charge density produced by the defect. Although this quantity can in principle be computed by our scattering theoretic methods, the practical difficulties are quite large. It is the difficulties associated

with these corrections which are the basis for our present view, and our proposals for further work, that computations of total energy changes associated with defects or with impurities may best be performed for atomic clusters.

Other work performed under partial support by this grant consisted of studies concerning density functional theory, and ferromagnetism of two-dimensional systems. We extended the previous work of Rajagopal and Ray and evaluated the second gradient correction to the exchange-correlation energy of an inhomogeneous electron gas. It was very helpful in establishing the validity of gradient expansion and is an essential ingredient in the calculation of surface energy of a metal-vacuum interface.

The work on two dimensional systems examined the ground state energy of four different systems (ideal 3-D electron gas, ideal 2-D electron gas, quasi 2-D electron system resembling electrons trapped on a liquid-helium surface and quasi 2-D electron system resembling inversion layers of the $Si(100)-SiO_2$ system e.g. MOSFET system) for all magnetizations and a wide range of electron densities. We found that the transition from nonmagnetic to ferromagnetic state is abrupt (as a function of electron density) in the case of ideal 2-D electron gas and that of electrons on liquid helium surface but gradual in the other two cases.

Although a definitive calculation of the vacancy formation energy has not been achieved, the results obtained so far do have considerable scientific importance: The items of greatest significance for the defect problem are:

(1) The calculation of atomic displacements around vacancies and interstitials. This should be useful to all further studies of defects in aluminum.

(2) The calculation of scattering phase shifts and the change in single particle energies, which is an essential ingredient in assessing the energetics of defect formations.

(3) The demonstration of the importance of exchange and Coulomb corrections in considering the total energy.

There are accomplishments which extend beyond the defect problem: These include:

(1) Demonstration that the LCGO method of band calculations using a local exchange potential is able to account for the charge distribution and Fermi surface in a multivalent, nearly free electron metal.

(2) Development of a formalism for the wave vector and frequency dependent dielectric matrix, followed by its actual calculation. This represents a significant extension of both theory and computational ability, and is likely to be a major contribution of enduring value to solid state physics.

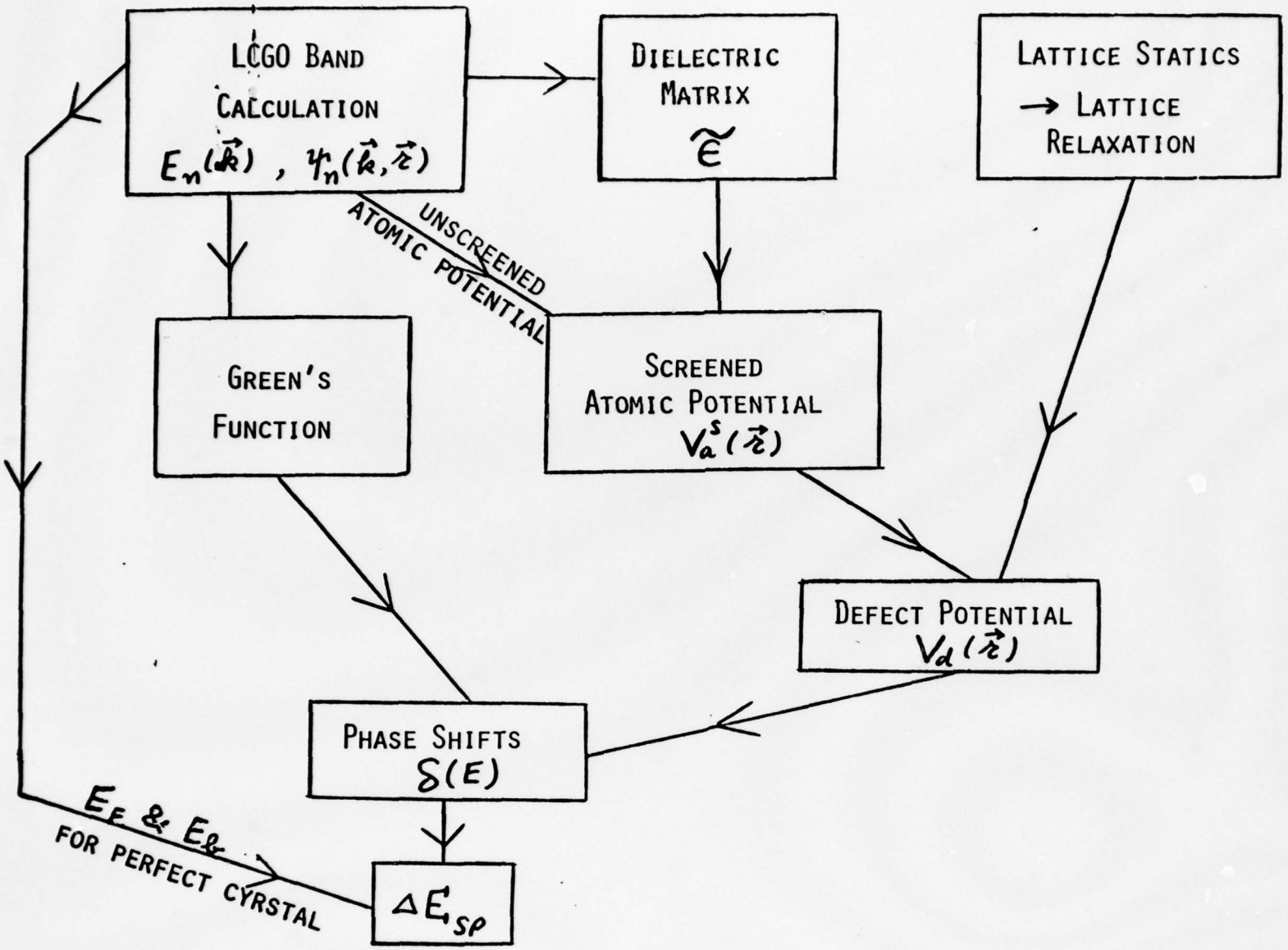

Fig. 1: Conceptual Organization of the Calculation

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Degrees Granted

None